Effect of Sintering Temperature on Mechanical Properties of Titanium Fiber Thin Plate Formed by Compression Shearing Method at Room Temperature

Noboru NAKAYAMA1, Hiroto TAMA2, Masaomi HORITA3, Hiroyuki MIKI4, Hideyuki UTSUMI5 and Hiroyuku TAKEISHI5

1 Department of Mechanical Systems Engineering, Shinshu University, Nagano 380-8553, Japan
2 Graduate School of Science and Technology, Shinshu University, Nagano 380-8553, Japan
3 Technical Division, Faculty of Engineering, Shinshu University, Nagano 380-8553, Japan
4 Frontier Research Institute for Interdisciplinary Sciences, Tohoku University, Miyagi 980-8578, Japan
5 Faculty of Engineering, Chiba Institute of Technology, Chiba 275-8588, Japan

(Received 10 January 2014; received in revised from 20 March 2014; accepted 19 April 2014)

Abstract
Titanium fiber thin plates were formed by the compression shearing method at room temperature, after which they were sintered. The effects of the number of strain applications (N) and the sintering temperature (T) on the sectional structure and mechanical properties of the formed samples were examined. Normally, biomaterials are required to have a Young’s modulus and tensile strength that are equivalent to those of compact bone. The bonded area of the titanium fibers increased with sintering temperature, thus improving the mechanical properties. Moreover, the density of the titanium fiber thin plate increased with sintering temperature and number of strain applications. Titanium fiber thin plates with N=0, T=300–773 K; N=1, T=300–773 K; and N=4, T=300–573 K are suitable as biological materials because their Young’s modulus and tensile strength are equivalent to those of compact bone. Also, N=0–1, T=823–923 K and N=4, T=773–923 K may be used for aviation structural materials.

Key words
Titanium, Biomaterials, Plastic Working, Porous Material, Strength Properties

1. Introduction
Titanium has excellent biocompatibility, strength, and corrosion resistance, so it is commonly used as a biomaterial in the field of medicine. Normally, a biomaterial is required to have a Young’s modulus and tensile strength equivalent to compact bone, as well as an outstanding affinity to bone. Furthermore, biomaterials used to cover areas of missing skull bone (after skull fractures) and to prepare the form of a bone graft (after bone grafting) must be flexible.

However, rolled pure titanium has a higher tensile strength and a higher Young’s modulus than compact bone. Therefore, it is necessary to develop a titanium-based material that has a lower elastic modulus. One material that may satisfy the above requirements is a porous molded material containing solidified flexible titanium fibers. Therefore, a titanium fiber thin plate containing pores was formed by solidifying titanium fibers through the compression shearing method at room temperature (COSME-RT) [2-11]. COSME-RT is a method of solidifying metal powder and metal fibers at room temperature while applying a compression force and a shearing force. As a result, a titanium fiber thin plate that has a high surface roughness and mechanical properties similar to those of compact bone was developed [12]. However, the Young’s modulus and tensile strength of the titanium fiber thin plate were kept constant by changing the shearing distance.

The mechanical properties of compact bone depend on sex, age, geographic region, and individual characteristics. Therefore, it is desired to control the mechanical properties of the biomaterial. To change the tensile strength, it is necessary to change the bonding strength between the fibers. Therefore, it is considered that the tensile strength of the titanium fiber thin plate can be improved by sintering.

The purpose of the present study was to develop biomaterials based on titanium fiber thin plates with controlled mechanical properties. Titanium fiber thin plates were formed by COSME-RT using various numbers of strain applications. After formation, the plates were sintered at various sintering temperatures. The effects of the number of strain applications and the sintering temperature on the sectional structure and mechanical properties of the samples were examined, and the results are presented herein.

2. Sample Preparation
2.1 Material
In the present study, fibrous, 99.52% pure (ASTM Grade 1) titanium with a fiber diameter of approximately 20 µm was used for the solidification. Fibers with an aspect ratio (AR = diameter/height) of 100 were prepared. Figure 1 shows images of the titanium fiber. As shown in Fig. 1(b), the fiber has an asperity on its side.

(a) Low-magnification view  (b) High-magnification view

Fig. 1 SEM images of Ti fibers
2.2 COSME-RT
A schematic diagram of the COSME-RT process is shown in Fig. 2. First, pure titanium fibers are placed on a stationary plate. A moving plate is then placed on top of the stationary plate, and a compression stress \( \sigma_N \) is applied to the moving plate and maintained during the formation process. A shearing load is also applied to the moving plate, which is then displaced in the shearing direction.

The titanium fiber thin plate was fabricated by repeating this procedure. Since there is a risk that the plate will break due to the sudden application of a large strain, the formation process was performed repeatedly at a small strain level. The number of repetitions is referred to as the shearing number \( N \).

The target dimensions of the formed samples were approximately \( 0.6 \text{ mm} \times 40 \text{ mm} \times 10 \text{ mm} \). A 1.0 g mass of titanium fibers was used for each sample. The COSME-RT forming conditions were constant, and the following values were used: compression stress \( \sigma_N = 1000 \text{ MPa} \) (compression load, \( P_N = 400 \text{ kN} \)), shearing velocity \( v = 1 \text{ mm/min} \), and shearing distance \( L = 0.1 \text{ mm} \). The plates were formed using shearing numbers \( N = 0, 1, \text{ and } 4 \). The plate formed at \( N = 0 \) was compressed only.

Top-view images of the samples are shown in Fig. 3 for (a) \( N = 0 \), \( T = 300 \text{ K} \) (sintering temperature) and (b) \( N = 4 \), \( T = 300 \text{ K} \). A metallic luster was obtained on the sample surface by increasing the shearing number. It is thought that the friction was occurred during die and Ti fibers with increasing the shearing number.

2.3 Forming conditions
The titanium fiber thin plate was formed using a compression shearing apparatus (Dip, DRD-NNK-001). The target dimensions of the formed samples were approximately \( 0.6 \text{ mm} \times 40 \text{ mm} \times 10 \text{ mm} \). A 1.0 g mass of titanium fibers was used for each sample. The COSME-RT forming conditions were constant, and the following values were used: compression stress \( \sigma_N = 1000 \text{ MPa} \) (compression load, \( P_N = 400 \text{ kN} \)), shearing velocity \( v = 1 \text{ mm/min} \), and shearing distance \( L = 0.1 \text{ mm} \). The plates were formed using shearing numbers \( N = 0, 1, \text{ and } 4 \). The plate formed at \( N = 0 \) was compressed only.

Top-view images of the samples are shown in Fig. 3 for (a) \( N = 0 \), \( T = 300 \text{ K} \) (sintering temperature) and (b) \( N = 4 \), \( T = 300 \text{ K} \). A metallic luster was obtained on the sample surface by increasing the shearing number. It is thought that the friction was occurred during die and Ti fibers with increasing the shearing number.

2.4 Sintering
In order to bond the titanium fibers, the plates were sintered. Sintering was started from room temperature. The sintering temperatures were \( T = 573, 773, 823, 873, \text{ and } 923 \text{ K} \), and sintering was performed in a vacuum (4 \(^3\text{Pa}) for one hour. Sintering temperature was decided near recrystallization temperature of titanium (=\(773\text{K}\)). Heating was performed using a heater. Therefore, no compression stress was added during sintering. Top-view images of the samples are shown in Fig. 4 for (a) \( N = 4 \), \( T = 773 \text{ K} \) and (b) \( N = 4 \), \( T = 873 \text{ K} \). The plate thickness did not change as a result of the sintering process, and the appearance of the samples did not change after sintering was performed.

![Fig. 4 Top-view images of the sintered samples (N=4)](image)

3. Experimental Procedures
3.1 Cross-sectional observation
In order to investigate the cross-sectional structure of the samples, cross sections of the samples were observed by field-emission scanning electron microscopy (FE-SEM; JSM-7000F, JEOL Ltd.). Figure 5 shows lower-magnification cross-sectional SEM images of the plates formed at (a) \( N = 0 \), \( T = 300 \text{ K} \); (b) \( N = 1 \), \( T = 300 \text{ K} \); (c) \( N = 4 \), \( T = 300 \text{ K} \); (d) \( N = 4 \), \( T = 773 \text{ K} \); (e) \( N = 4 \), \( T = 823 \text{ K} \); and (f) \( N = 4 \), \( T = 873 \text{ K} \). In the samples shown in Fig. 5(a) through 5(c), the plates have pores, and the titanium fibers are not bonded. Figure 5(c) through (f) shows that the porosity of the plates was reduced by an increasing in the sintering temperature and shearing number.

Figure 6 shows higher-magnification cross-sectional SEM images of the plates formed at (a) \( N = 4 \), \( T = 300 \text{ K} \); (b) \( N = 4 \), \( T = 773 \text{ K} \); (c) \( N = 4 \), \( T = 823 \text{ K} \); and (d) \( N = 4 \), \( T = 873 \text{ K} \). The titanium fibers became more fully bonded as the sintering temperature was increased.

![Fig. 5 Lower-magnification cross-sectional SEM images](image)
3.2 Density measurement

In order to investigate the relative density of the titanium fiber thin plates, cross-sectional SEM images of the samples were processed using a motion analysis microscope (VW-6000, Keyence Co., Ltd.). The relative density was defined as the ratio of the area of the fiber portion of the plate to the total area of the plate.

The relationship between the sintering temperature and the relative density is shown in Fig. 7. The relative density of the plates was increased by sintering, and also as the shearing number increased. Because the fibers are in close contact with the increase the shearing number, density is improved. It is thought that the relative density was enhanced by increasing total shearing strain.

3.3 Tensile test

In order to investigate the mechanical properties of the plates, the sintering temperature was varied, and tensile testing was performed using a tabletop tensile test machine (AGS-5kN, SHIMADZU Co., Ltd.). The sample dimensions are shown in Fig. 8. The test machine was operated at a tensile velocity of 0.5 mm/min. Strain gauges 2 mm in length (KFG-2N-120-C1-11, KYOWA ELECTRONIC INSTRUMENTS CO., LTD.) were affixed to both sides of the parallel portion of the test sample. The strain was measured by the two-active-gauge method. The Young's modulus was calculated based on the strain gauge readings.

Figure 9 shows the load–distance curve for (a) $N = 0$, (b) $N = 1$, and (c) $N = 4$. For comparison, the load–distance of rolled Ti is also shown in Fig. 9.

The tensile strength was calculated based on Fig. 9. The relationship between the sintering temperature and...
the tensile strength is shown in Fig. 10. Figure 10 reveals that the tensile strength of the plates increased with sintering temperature. The tensile strength of the samples was 0.18–0.57 times that of rolled Ti. Therefore, titanium material having a low strength was obtained. The tensile strength of the samples for $N = 0$, $T = 300–823$ K; $N = 1$, $T = 300–773$ K; and $N = 4$, $T = 300–573$ K was equivalent to that of compact bone. The tensile strength of the $N = 0$, $T = 873–923$ K; $N = 1$, $T = 823–923$ K; and $N = 4$, $T = 773–923$ K samples was 1.3–2.5 times that of compact bone. Thus, the $N = 0$, $T = 300–823$ K; $N = 1$, $T = 300–773$ K; and $N = 4$, $T = 300–573$ K samples are suitable as biomaterials from the viewpoint of tensile strength.

Fig. 10 Relationship between sintering temperature and tensile strength

The relationship between the sintering temperature and the Young’s modulus is shown in Fig. 11, which indicates that the Young’s modulus of the plates increased with sintering temperature. The Young’s modulus of the samples was 0.14–0.77 times that of rolled Ti. Therefore, titanium material having a low strength was obtained. The Young’s modulus of the samples for $N = 0$, $T = 300–773$ K; $N = 1$, $T = 300–773$ K; and $N = 4$, $T = 300–573$ K was equivalent to the Young’s modulus of compact bone. The Young’s modulus of the $N = 0$, $T = 873–923$ K; $N = 1$, $T = 823–923$ K; and $N = 4$, $T = 773–923$ K samples was 1.3–3.5 times that of compact bone. Thus, the $N = 0$, $T = 300–773$ K; $N = 1$, $T = 300–773$ K; and $N = 4$, $T = 300–573$ K samples are suitable as biomaterials from the viewpoint of the Young’s modulus.

From the above results, it is possible to control the tensile strength of titanium fiber thin plates within a range of 0.7 to 2.5 times that of compact bone. It is also possible to control the Young’s modulus within a range of 0.67 to 3.5 times that of compact bone. Lastly, the tensile strength and Young’s modulus of the $N = 0$, $T = 300–773$ K; $N = 1$, $T = 300–773$ K; and $N = 4$, $T = 300–573$ K samples were equivalent to those of compact bone. Therefore, the $N = 0$, $T = 300–773$ K; $N = 1$, $T = 300–773$ K; and $N = 4$, $T = 300–573$ K materials are suitable as biological materials because they are in the range of the target value.

3.4 Fracture surface observation

The fracture surfaces of the samples were observed using FE-SEM. Figure 12 shows lower-magnification SEM images of the fracture surfaces for (a) $N = 4$, $T = 300$ K; (b) $N = 4$, $T = 773$ K; (c) $N = 4$, $T = 823$ K; and (d) $N = 4$, $T = 873$ K.

Fig. 11 Relationship between sintering temperature and Young’s modulus

Fig. 12 Lower-magnification SEM images of the fracture surfaces ($N=4$)

Fig. 13 Higher-magnification SEM images of the fracture surfaces ($N=4$)

Figure 11(a) reveals that some fibers came loose. Such fiber unraveling decreased with increasing sintering
temperature. Figure 12(c) and 12(d) shows the fracture surfaces in detail.

Figure 13 shows higher-magnification SEM images of the fracture surfaces for (a) \( N = 4, T = 300 \text{ K} \); (b) \( N = 4, T = 773 \text{ K} \); (c) \( N = 4, T = 823 \text{ K} \); and (d) \( N = 4, T = 873 \text{ K} \). Figure 13(a) shows that the fibers within the plate did not bind. However, as the sintering temperature increased, the contact between the fibers became closer. Binding of fibers was confirmed in the \( N = 4, T = 873 \text{ K} \) sample.

3.5 Mercury intrusion test

In order to investigate the porosity of the specimens in more detail, mercury intrusion tests were performed. A mercury intrusion test is a porosity test that utilizes the large surface tension characteristics of mercury [13]. The porosity and pore diameter of the specimens can be determined from the cumulative volume and the applied pressure of the mercury.

Figure 14 shows that the typical relationship between cumulative volume and the applied pressure of the mercury for \( N = 4 \). It can be seen that the rapidly increased of mercury volume, and after slightly increased as a function of pressure. Pore radius and total cumulative volume was calculated from changing behavior of Fig. 14.

![Fig. 14 Typical result of mercury intrusion test for \( N = 4 \)](image)

Figure 15 shows the relationship between the sintering temperature and the total cumulative volume. The total cumulative volume decreased with increasing sintering temperature. The total cumulative volume is equal to the total void volume in the sample. Therefore, the total void volume in the sample decreases with increasing sintering temperature. Figure 16 shows the relationship between the sintering temperature and the average pore radius. The average pore radius was stable.

![Fig. 15 Relationship between sintering temperature and total cumulative volume](image)

![Fig. 16 Relationship between sintering temperature and average pore radius](image)

The total cumulative volume was decreased with increasing sintering temperature. However, average pore radius was stable. It is thought that the pore of titanium thin plate was decreased by bond of fiber boundary as shown in Fig. 5 and 6.

4. Considerations

In the present study, titanium fiber thin plates formed by COSME-RT were sintered. Their mechanical properties (Young’s modulus and tensile strength) improved with increasing sintering temperature, and their density increased. Therefore, the improvement in the mechanical properties of the plates is related to the internal structure.

Bonding methods in which metal fibers are in close contact with each other at high temperatures are diffusion bonding methods [14]. Bonds are produced by diffusion of the atoms of the base material. Titanium can bond without leaving any voids when diffusion bonding is used. Furthermore, the surface oxide film is dispersed in the base material [15]. In addition, diffusion of oxygen into the titanium base material becomes significant at 870 K [14].

Based on the above considerations, the bonded area of the titanium fibers is considered to have increased with sintering temperature at and above 800 K, and this is confirmed by Fig. 6. Therefore, the mechanical properties of the plates improved with increasing sintering temperature.

5. Conclusion

The purpose of the present study is to develop a biomaterial with controllable mechanical properties. Titanium fiber thin plates were formed using COSME-RT with different shearing numbers. After formation, the plates were sintered at various temperatures. The effects of the shearing number and the sintering temperature on the cross-sectional structure and the mechanical properties of the samples were examined, and the following results were obtained:

1. The relative density of the plates increased as a result of sintering.
2. The mechanical properties (tensile strength and Young’s modulus) improved with increasing sintering temperature. It was possible to control the tensile strength to within a range of 0.7 to 2.5 times that of compact bone. Also, it was possible to control the
Young’s modulus to within a range of 0.67 to 3.5 times that of compact bone.

(3) The void volume decreased with increasing sintering temperature, and the average pore radius increased above 800 K.

Based on the above results, the titanium fiber thin plates with $N = 0$, $T = 300–773$ K; $N = 1$, $T = 300–773$ K; and $N = 4$, $T = 300–573$ K are suitable as biological materials because their Young’s modulus and tensile strength are equivalent to those of compact bone. Therefore, a biomaterial that can be used in a variety of bones was developed.

Nomenclature

COSME-RT Compression shearing method at room temperature

$L$ Shearing distance

$N$ Shearing number

$T$ Sintering temperature

$\sigma$ Compression stress

$v$ Shearing velocity

Acknowledgement

The present research was supported by the Program for Fostering Regional Innovation in Nagano through MEXT, Japan.

References


